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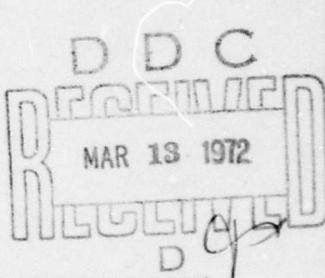
AFATL-TR-71-136

DEVELOPMENT OF EXPERIMENTAL
INTERMETALLIC-FORMING STARTER SYSTEM
FOR THE
M1 SMOKE (HC) CANISTER

FLAME, INCENDIARY, AND FUEL-AIR EXPLOSIVES BRANCH
FLAME, INCENDIARY, AND EXPLOSIVES DIVISION

TECHNICAL REPORT AFATL-TR-71-136

OCTOBER 1971



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**Development of Experimental
Intermetallic-Forming Starter System
for the
M1 Smoke (HC) Canister**

Robert L. McKenney, Jr.

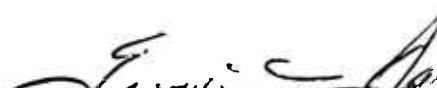
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FOREWORD

At the request of Edgewood Arsenal (SMUEA/DEMG), the Incendiary Laboratory of the Air Force Armament Laboratory, Eglin Air Force Base, Florida, became actively engaged in a program to develop an improved starter system for the M1 smoke (HC) canister. Funds were allocated under MIPR No. A11HS12501F4UB. The program was worked between May and August 1971 as a part of Project 1082, Task 01, Work Unit 001 at the Air Force Armament Laboratory.

This technical report has been reviewed and is approved.


FRANKLIN C. DAVIES, Colonel, USAF
Chief, Flame, Incendiary, and Explosives Division

ABSTRACT

A program was initiated to develop an improved starter system for the M1 smoke (HC) canister used in the 105mm M84A1 (HC) smoke projectile. The experimental starter material was based on an intermetallic-forming reaction of the titanium-boron system. Static and dynamic testing was carried out. The starter system produces the heat necessary to initiate and sustain combustion of HC smoke composition.

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SECTION I

INTRODUCTION

This report describes the work done by the Air Force Armament Laboratory (AFATL) in developing an intermetallic-forming, pelletized, starter system to be tested in the M1 smoke (HC) canister. This canister is used in conjunction with the 105mm M84A1 (HC) smoke projectile. A projectile loaded with three conventional M1 smoke (HC) canisters is shown in Figure 1 and a canister is shown in Figure 2.

When the projectile is fired from the 105mm howitzer, the canisters are subjected to both longitudinal and radial set-back forces of approximately 14,000 and 7,000 psi, respectively. These forces are sufficient to expand the canisters radially until they are firm against the inner wall of the projectile. There is a delay of approximately 8 to 55 seconds between launching of the projectile and functioning of the canister expelling charge. The expelling charge consists of 50.5 grams of class A-3 black powder, which provides the energy required for ignition of the starter composition material and for ejection of the canisters from the incoming projectile at some predetermined height, usually 1,100 to 3,000 feet. The pressure buildup within the projectile must be sufficient to rupture the two threads on the projectile base-plate (Figure 1) and to force out the tightly fitting canisters. To facilitate the ejection process, a baffle plate is incorporated between the nose canister and black powder charge, and major pressure buildup is on the black powder side of this baffle plate. After the expelling charge functions, the dwell time of the canisters in the projectile is in the millisecond range, and it is during this time that the canister starter systems are ignited.

The Starter Mixture (Dry) II (Chemical Corps Formula) normally incorporated in the finished canisters remains in an essentially loose granular state. The loose granular condition of the starter mixture, coupled with the tremendous setback forces encountered by the system at the time the projectile is launched, was thought to be the cause of an unusually high dud rate. Therefore, a change was required in the starter composition and/or configuration. A cutaway drawing of a conventional M1 smoke (HC) canister is shown in Figure 2.

The exothermic nature of certain intermetallic-forming reactions, including boride-forming mixtures, has previously been established (References 1 and 2). These systems are generally of tailorable energetics, highly reliable, moderately easy to initiate, and safe to handle once configured. These intermetallic-forming mixtures react without forming a significant vapor phase, they do not require the presence of oxygen in any form during the course of the reaction, and they can produce intense radiant heat.

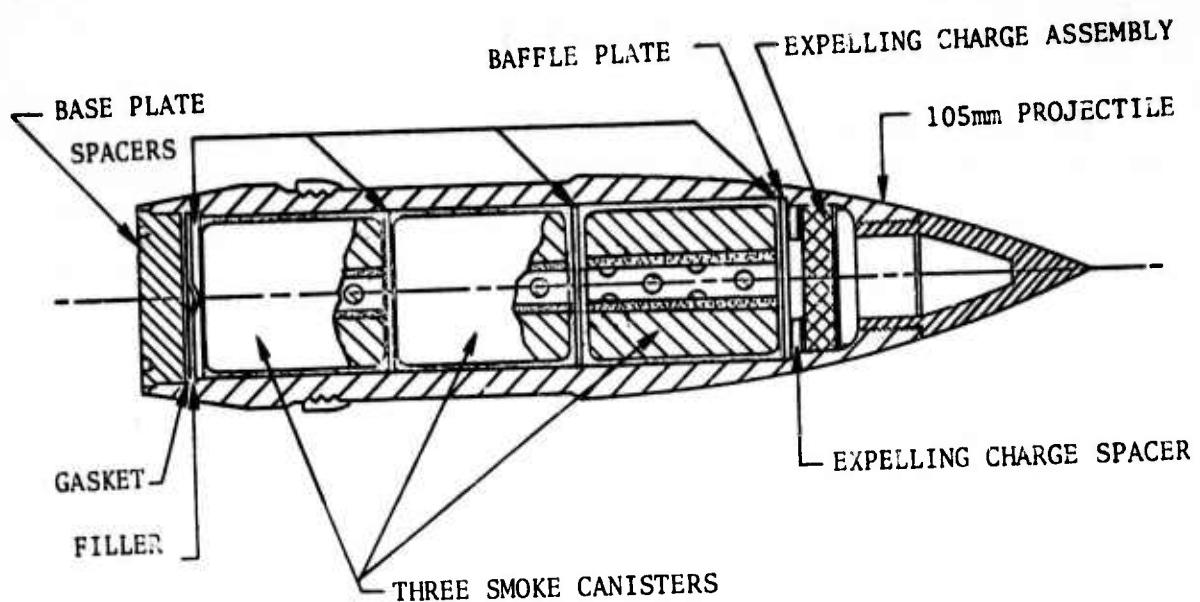


Figure 1. Sideview of the 105mm M84A1(HC) Smoke Projectile Loaded with Conventional M1 smoke (HC) Canisters

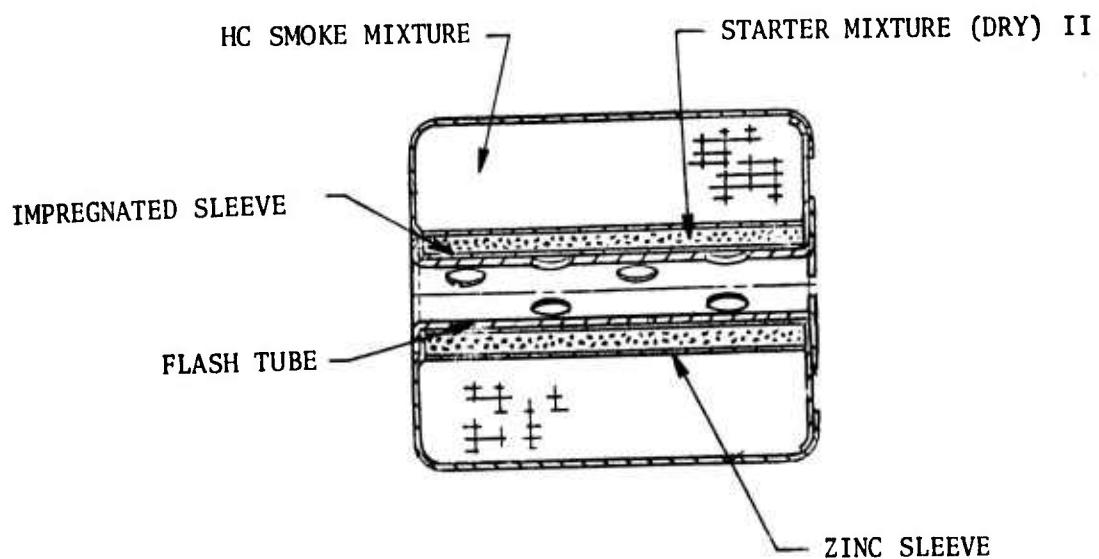


Figure 2. Conventional M1 Smoke (HC) Canister

Titanium and boron were chosen as the basic ingredients for the starter system for the following reasons:

1. The mixture is easily pressed into various shaped bodies that have reasonable strength without the addition of a binder.
2. Ignition can be afforded with relative ease because of low thermal conductivity.
3. A high heat of reaction (approximately 1200 cal/gm) in air or inert atmosphere is obtained for the formation of TiB_2 .
4. A high linear reaction rate is provided, generally varying from 50 to 1000 msec/cm depending on the particle size range of the components and the bulk density.
5. The desirable characteristics include tailorable chemical and physical properties.
6. A high temperature (2000° to $3000^\circ C$) is provided at one atmosphere of air.
7. Reactivity is reliable under variable pressures including those greater than one atmosphere.
8. A hard reaction product is formed with dimensions similar to that of the pre-reaction configuration.

SECTION II

EQUIPMENT AND MATERIALS

Calorimetric values were obtained by standard Parr bomb technique using an Adiabatic 1241 Calorimeter (Parr Instrument Company). When ignition was not afforded by the standard method, a pellet with a known amount of a first-fire material was used. That portion of the total heat output attributed to the first-fire is subtracted from the total, and the remainder is designated as the heat of reaction of the system (Reference 3).

Ignition temperatures were measured by the differential thermal analysis technique using a Mettler Recording Vacuum Thermoanalyzer. All measurements were made on loose or tamped powders contained in 3 by 4 millimeter dense alumina crucible liners. The atmosphere immediately around the sample was dry air or argon flowing at 5.7 to 6.0 liters/hour. A heating rate of 15°C/minute was used in all cases. A standard micro differential thermal analysis (DTA) sample holder with Pt/Pt-Rh10 thermocouples (reference temperature maintained at 25°C) was used. Norton Alundum "RR" (Blue Label), 60 mesh, was used a reference material. Temperature calibration was accomplished with National Bureau of Standards (NBS) standard metals (tin, 42f; lead, 49e; zinc, 740; aluminum 44e; and copper, 45d) covering the range 232° to 1083°C and other high purity (99.999%) metals (silver, nickel rod; and palladium rod).

HC smoke composition material was studied by differential thermal analysis technique. Unless otherwise stated, all samples were premixed, loaded into soft glass capillary tubes in an argon atmosphere, and sealed with a torch. The unreacted mixture was heated at 4°C per minute to a maximum temperature of 540°C. Where applicable, the reaction residue was reheated to the same temperature at 10°C per minute. No rigorous conditions were established to insure that the samples selected for analysis were representative.

Drop-weight measurements were made with a Technoproduts Drop-Weight Tester, Model 7. All tests were performed on 20-mg loose samples contained in brass cups of 0.312 inch diameter. The diameter of the steel plunger tip was 0.304 inch. The test consisted of dropping variable weights, 6 kg maximum, from variable heights, 50 cm maximum.

The photocell technique described in Reference 4 was used to obtain linear burn rate values from samples compacted into a bar shape. The bars, 0.25 by 0.25 inch cross section, were 2.5 inches long and weighed approximately 6 grams. Compaction to 25.6×10^3 psi was effected normal to the long axis.

Maximum reaction temperatures were measured with an infrared thermometer (Thermodot) Model TD-17, Infrared Industries, Incorporated. The instrument, which has a spectral range 1.75 to 2.7 microns, was operated on an arbitrary emissivity setting of 0.5. Test sample dimensions were 0.5 inch diameter and 0.5 to 0.6 inch long. The applied pelletizing pressure was 25×10^3 psi. Pellets were usually prepared with a top layer consisting of 0.25 gram of first-fire material, which was ignited by a hot nichrome wire.

The materials used in this program include titanium that is characterized by irregular-shaped particles and two types of amorphous boron, 90 to 92 percent grade. One type of boron is of 10 micron effective particle size, and the other, which meets the requirements of MIL-B-5192 (ORD), is of 1 micron average particle size. All of these materials were used as received. Barium chromate and potassium nitrate were selected as sensitizing materials. Each of the oxidizers underwent special treatment either prior to or after mixing with the metal components.

SECTION III

STARTER MIXTURE CONFIGURATION AND COMPOSITION

Because of the burning characteristics of the titanium-boron system, it was anticipated that only a relatively small amount of this mixture would be required to ignite and cause sustained burning of the HC smoke composition. As a result, the AFATL starter composition material was configured into a tube-shaped pellet as shown in Figure 3. The compaction pressure was approximately 25×10^3 psi and resulted in an average pellet that was 1.26 inches in outside diameter, 0.68 inch in height, 22 grams in mass, and with a 0.66 inch diameter center hole.

Two starter pellet configurations were developed for evaluation in the M1 smoke canister. The initial system, Starter Mixture A, consisted of an outer core of a titanium-boron mixture and an inner core of a titanium-boron-barium chromate mixture. The second system, Starter Mixture B, consisted primarily of titanium and boron with a small amount of potassium nitrate added as a sensitizer. The dimensions of the Starter Mixture B pellet were identical to those of Starter Mixture A. There was no requirement for a sensitized inner core in a pellet prepared from Starter Mixture B because the mixture itself was sensitized to ignition.

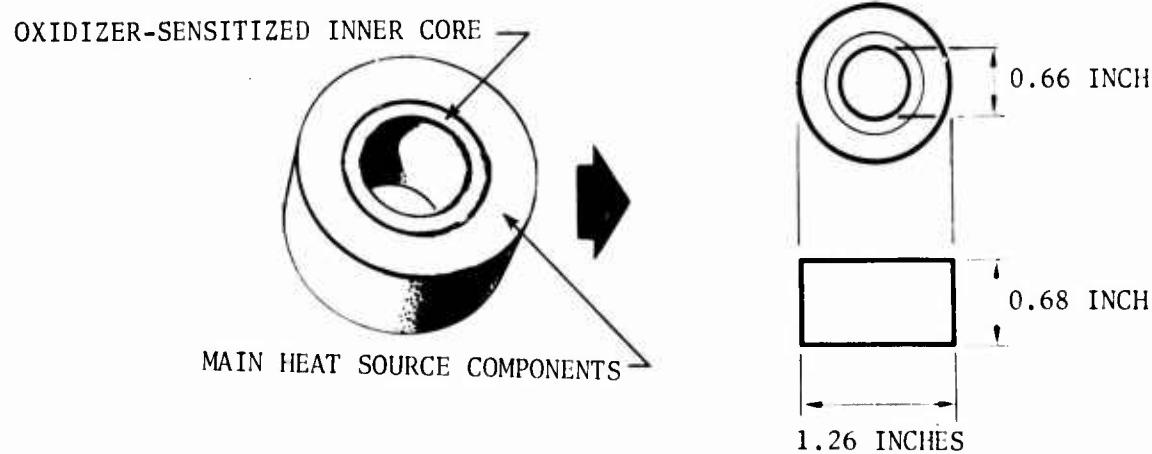


Figure 3. AFATL Starter Pellet Showing Concentric Configuration of the Main Heat Source System and the Oxidizer-sensitized Inner Core

The Starter Mixture A system was composed of an oxidizer sensitized inner core and an intermetallic-forming outer core in the weight ratio, 0.3:0.7. The composition of the inner core was 74 percent (by weight) barium chromate; 18 percent (by weight) titanium, -325 mesh (10 micron nominal particle size); and 8 percent (by weight) amorphous boron, 90 to 92% grade (1 micron maximum average particle size). No weight compensation was made for the impurities in the boron. The outer core was composed of 69 percent (by weight) titanium, -325 mesh (10 micron nominal particle size), and 31 percent (by weight) amorphous boron, 90 to 92% grade (10 micron effective particle size). The three components of the inner core were mixed in a ball mill until the mixture became olive-drab in color and relatively free of agglomerates of yellow barium chromate. Since the mixture tended to accumulate on the sides of the jar during the milling operation, it was essential for the material to be scraped intermittently from the walls. The outer core components were blended by a standard mixing apparatus. The physical properties of Starter Mixture A are shown in Table I.

TABLE I. PHYSICAL PROPERTIES OF STARTER MIXTURE A

| CORE | CALORMETRIC OUTPUT IN AIR Cal/Gm | PRESSURE/Atmospheres |
|---|--|----------------------|
| TOTAL | 1111 (± 6) 1570 (± 33) | 2 30 |
| INNER | 663 (± 6) 748 (± 4) | 2 30 |
| OUTER | 902 (± 3) 1364 (± 33) | 2 30 |
| DTA Ignition Temperature (Air or argon atmosphere) | 700° to 750° C | (Inner Core) |
| Maximum Reaction Temperature (Measured on the exposed surface of the outer core material at an arbitrary emissivity setting of 0.5) | 2,000° to 2,600° C | |
| Linear Burn Rate: Inner Core Outer core | 0.025 (± 0.001) sec/cm 0.13 (± 0.02) sec/cm | |
| Bulk Density | 2.2 gm/cc | |
| Impact Sensitivity (Measured separately on both inner and outer core materials) | > 300 kg-cm | |

The Starter Mixture B system was a sensitized intermetallic-forming mixture consisting of 3 percent (by weight) potassium nitrate, -297 micron (material passed through an NBS No. 50 screen); 67 percent (by weight) titanium, particle size range +30 mesh (less than 1 percent (by weight), -100 mesh (44 percent (by weight), and -325 mesh (4.2 \pm 0.5 percent (by weight), and 30 percent (by weight) amorphous boron, 90 to 92% grade (1.0 micron maximum particle size). The components were blended by a standard mixing apparatus. The potassium nitrate was dried before blending, and the mixture was stored over a desiccant. The physical properties of Starter Mixture B are shown in Table II.

TABLE II. PHYSICAL PROPERTIES OF STARTER MIXTURE B

| ATMOSPHERE | CALOMETRIC OUTPUT, Cal/Gm | PRESSURE, Atmospheres |
|---|------------------------------|--------------------------|
| Air | 955 (\pm 6) | 2 |
| Argon | 746 | 1 |
| DTA Ignition Temperature: | >440°C (Air) | |
| Maximum Reaction Temperature: (Measurement made on the outer surface of the pellet at an arbitrary emissivity setting of 0.5) | 2760°C | |
| Linear Burn Rate: | 0.17(\pm 0.02) sec/cm | |
| Bulk Density: | 2.0 gm/cc | |
| Impact Sensitivity: | > 300 kg-cm | |

The DTA ignition temperature in Table II is based on experiments involving the Ti-B-KNO₃ system of various component ratios which indicate that initial reaction occurs between boron and potassium nitrate. It is evident, however, that the energy evolved from the boron-potassium nitrate reaction in Starter Mixture B is not sufficient to initiate the intermetallic-forming reaction (Ti+2B TiB₂) under DTA-type experimental conditions. Nonetheless, the exotherm associated with the reaction was readily seen in the thermogram. The intersection of straight lines drawn along the normal baseline and along the leading edge of the exotherm occurred at 440°C. Even though initiation of the main intermetallic-forming reaction did not occur, the mixture was definitely sensitized because ignition by the hot wire technique was readily accomplished. The pure titanium-boron system in the atomic ratio 1:2 was not readily ignited by this technique.

Starter Mixture A was tested statically and dynamically in the M1 smoke canister. Some of the results from these tests (discussed in Sections VI and VIII), along with cost considerations, led to the development of Starter Mixture B. However, prior to field-testing Starter Mixture B, the participation of the Air Force Armament Laboratory in the starter system improvement program was terminated.

Both Starter Mixtures A and B were compacted as single units in one pressing operation. The inner and outer core materials of Starter Mixture A were simultaneously loaded into a special mandril-equipped die (Figure 4) with the aid of a thin-walled separation tube which temporarily separated the two concentric cores. After loading was completed, the tube was removed and the loose material was compressed to 25×10^3 psi. Starter Mixture B was simply loaded into the mandril-equipped die and compacted to the same pressure. The resulting pellets of both starter mixtures were then coated with clear lacquer for easy handling and increased surface strength.

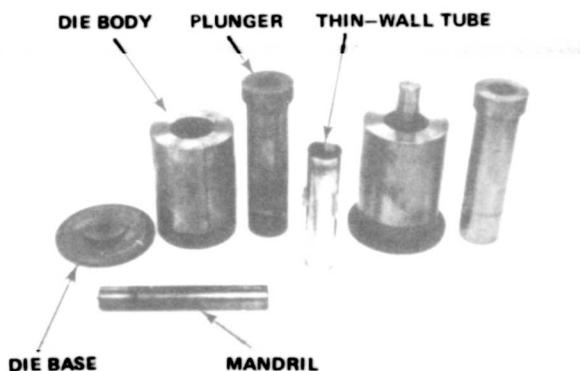


Figure 4. Components of the Die Used for Consolidation of Starter Mixtures A and B

SECTION IV

M1 CANISTER DESIGN CHANGES

An analysis of the probable causes for the inconsistent functioning of the conventional canisters and the ultimate strength of a compressed titanium-boron pellet indicated that compacted, unsupported, titanium-boron starter composition material would not survive setback forces encountered at the time of dynamic testing. Therefore, the design of the M1 canister metallic components was not changed. Two major changes were incorporated into the canister consumable components: (1) the removal of the zinc sleeve that separates the old, uncompacted, starter mixture from the HC smoke composition, and (2) the replacement of the impregnated sleeve with a Mylar[®] sleeve. This impregnated or Mylar[®] sleeve covers the canister flash tube and separates it from the starter and smoke-producing components of a filled canister (Figure 2). The primary purpose of the sleeve is to prevent loss of starter and/or HC smoke composition through the flash tube holes at all times, including the dynamic firing sequence.

This sleeve change was necessary because the conventional impregnated sleeve was rupturing at the flash tube hole sites. This phenomenon, commonly referred to as the "cookie-cutter effect", apparently occurs predominately at the bottom two sets of holes when setback forces are encountered. The starter mixture can then be forced through the holes into the flash tube void, resulting in insufficient energy for proper ignition of the HC smoke composition.

SECTION V

INCORPORATION OF STARTER SYSTEM INTO EXPERIMENTAL CANISTER

Since each starter pellet was prepared as an entity, it could be inspected and spot-tested prior to the filling of the canisters. The procedure for loading an experimental canister is shown in Figure 5. The first step was the insertion of a Mylar® sleeve, approximately 0.001 inch nominal thickness, over the canister flash tube. The starter pellet was then inserted over the sleeve to the base of the canister. The pellet was topped with a tight-fitting Mylar® or paper washer such that particles of the HC smoke composition could not fall between the loose-fitting pellet and the sleeve. The HC smoke composition was then added and consolidated in two steps in accordance with specification MIL-C-003298F(MU), Section 3.2. Then the canister was sealed and made ready for testing.

Little or no downward reconsolidation of the starter pellet occurred during HC smoke composition compaction. The starter pellet, however, was reconsolidated radially. The extent of radial reconsolidation was limited by both the steel flash tube and the mandril inserted into the flash tube during the pressing operation. In the final configuration, the starter pellet was in intimate contact with the HC smoke composition and protruded slightly through the lower set of Mylar® covered holes in the flash tube (Figure 6). It was demonstrated that the Mylar® readily expands through the holes and thereby holds the starter mixture firmly in place. The slight protrusion of the starter mixture into the flash tube void ideally exposed it to the initiation heat source.

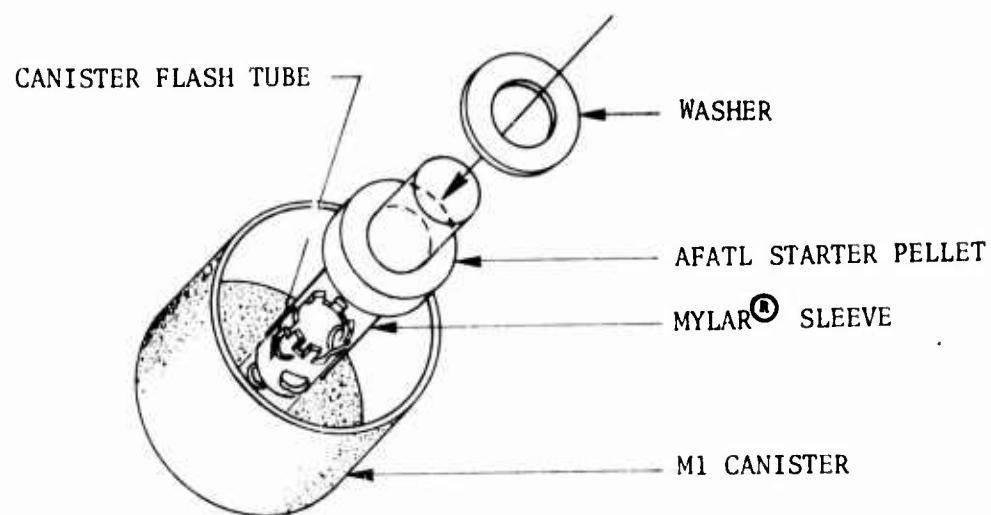


Figure 5. Loading Sequence for the M1 Smoke (HC) Canister with AFATL Improved Starter Pellet

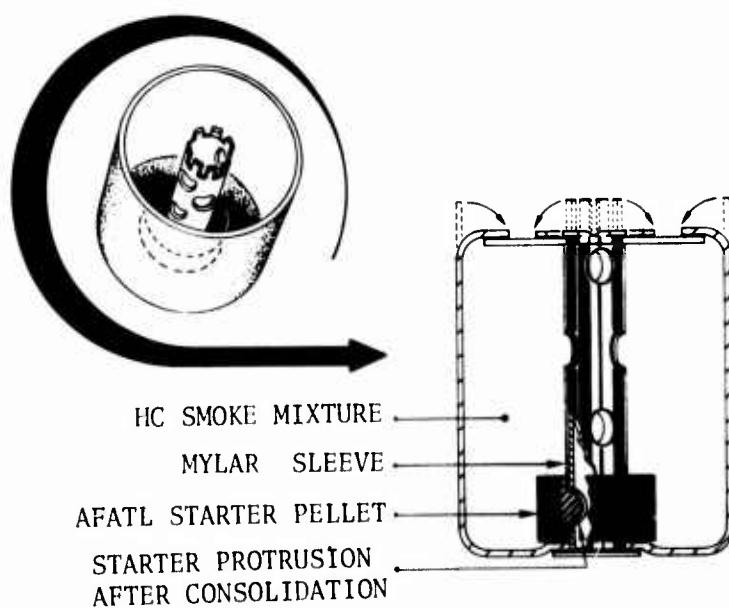


Figure 6. A Loaded M1 Smoke (HC) Canister Containing an AFATL Starter Pellet

SECTION VI

STATIC TESTING

Several static tests were conducted at Edgewood Arsenal using canisters loaded with starter pellets prepared at the Air Force Armament Laboratory. Static testing consisted of firing loaded projectiles in an inverted, stationary position. The base of the projectile, the end from which the canisters are expelled, was pointed upward so the canisters would be ejected into the air. The nose of the projectile was resting on a steel base plate and fastened to a stake at a slight angle such that the canisters were released downrange. The expelling charge was fired with an electric squib. The canisters, although held snugly in place longitudinally by spacers, were relatively loose radially at the time of firing. This condition is drastically different from that encountered in a dynamic test where the canisters are expanded tightly against the projectile inner wall as a result of setback forces. Consequently, the canister dwell-time in the projectile after the expelling charge functions will be shorter for statically fired canisters than for those fired dynamically. As a result, the time that the starter material is exposed to the heat produced by the reacted black powder will be much less for statically fired canisters. The ultimate consequences of this condition, which will be discussed later, cause the usefulness of static testing to be questioned, except for providing the most empirical of data.

Early in the static testing program, it became evident that the baffle plate in the test projectile was shielding the exposed portions of the starter pellets from a considerable portion of the energy released by the expelling charge. It also became apparent that the intermetallic-forming mixture of titanium and boron (1:2 atomic ratio), used in the initial testing, must be sensitized on the surface protruding into the flash tube before reliable ignition will occur. Even though the amount of energy imparted to the starter pellets in a statically fired system is not known, it has been shown to decrease from nose to base canister and not be of sufficient intensity to reliably ignite the unsensitized intermetallic-forming system chosen for this project. The nose canister is adjacent to the expelling charge.

Starter Mixture A was developed and incorporated into the M1 canister for static testing. These tests were carried out both with and without baffle plates installed and at the prescribed temperatures of -50°, +70°, and +145°F. The tests showed that even with this sensitized system, the baffle plate had to be eliminated to get reliable ignition in the base canister under static conditions. Without the baffle plate installed, all canisters functioned effectively over the stated temperature range. The HC smoke composition was observed to be burning vigorously upon ejection from the anchored projectile, and the performance of the individual canisters was not hindered by adverse field conditions on impact, such as

in deep mud or water. The smoke generated from any one canister was of sufficient density for screening or marking. As a direct result of these favorable results, Starter Mixture A was chosen for dynamic testing. A sufficient quantity of starter pellets was prepared from Starter Mixture A to load 45 canisters.

Prior to the all-up testing of the experimental canisters in the 105mm round, an effort was begun to design a pellet that could be more easily manufactured. The effort resulted in development of Starter Mixture B, which is basically an intermetallic-forming system sensitized by the addition of 3 percent (by weight) potassium nitrate. The product is hard and retains essentially the integrity of the initial shape, and as can be readily predicted, this is only one of many possible component combinations. The static testing of Starter Mixture B was delayed pending the outcome of a dynamic test in which Starter Mixture A was used.

SECTION VII

EDGWOOD ARSENAL IMPROVED STARTER SYSTEM

The improvement of the Edgewood starter system was a twofold process accomplished at the Edgewood laboratories. It involved the consolidation of conventional Starter Mixture (Dry) II into a tube-shaped pellet of considerable strength. This was accomplished with the aid of soluble nitrocellulose binder. The length of the pellets was such that two would extend the entire length of the flash tube in a sealed canister. Although the overall loading sequence is different, the Edgewood pellets are fitted around the Mylar[®] covered flash tube in the same manner as the AFATL pellets. Radial reconsolidation of Edgewood pellets was also effected during the final topping operation.

In order to get maximum efficiency from the two starter pellets and to minimize the possibility of the "cookie-cutter effect" taking place at the flash-tube hole sites, the flash tube was redesigned. The four holes at the base of the tube were eliminated, thereby strengthening the starter mixture adjacent to the solid tube and concentrating the evolved heat into the HC smoke composition. The upper starter pellet was still exposed to the heat source required for ignition. The lower pellet was readily ignited by the upper pellet and the heat produced from the combination easily ignited the smoke composition.

SECTION VIII

DYNAMIC TESTING

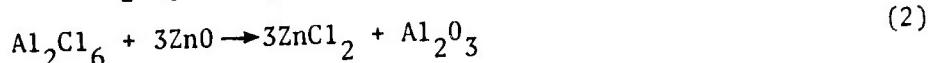
The dynamic tests consisted of live firing 77 experimental 105mm projectiles. Fifteen rounds were each loaded with three canisters containing HC smoke composition consolidated around Starter Mixture A. Five rounds each were conditioned at -50° , $+70^{\circ}$, and $+145^{\circ}\text{F}$ prior to firing. Baffle plates were not incorporated in any of the 15 rounds. At this time, the static test results indicated that a baffle plate was not required for the canister ejection process. The absence of the baffle plate would also result in more heat to the canister starter systems and afford reliable ignition. All of these rounds were loaded at Edgewood Arsenal. The other rounds in the test contained canisters in which various modifications were incorporated. These included 25 rounds containing canisters with the modified starter system developed by the Edgewood Arsenal.

The canisters containing Starter Mixture A did not perform well dynamically. The functioning canisters were characterized by poor smoke trails upon ejection from the incoming projectile and exceptionally long and erratic burn times. The base of each canister that functioned was bulged outward, and the bases of at least two canisters were ripped open. One round had no fuse action. Of the remaining 42 canisters, three were considered duds. The canisters containing the Edgewood Arsenal modified starter system and special four-hole flash tubes performed well. Since the starter mixture used by Edgewood Arsenal in their modified system is not an experimental material and is an in-house development, it was selected for future testing, and all testing with the AFATL experimental pellets was terminated.

SECTION IX

INVESTIGATION OF THE HC SMOKE COMBUSTION BY DIFFERENTIAL THERMAL ANALYSIS

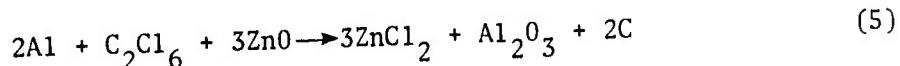
The erratic combustion of HC smoke composition ignited by Starter Mixture A under special test conditions led to a cursory qualitative investigation of the combustion process by differential thermal analysis (DTA). It is speculated (References 5 and 6) that the combustion process might proceed through the following steps:



or



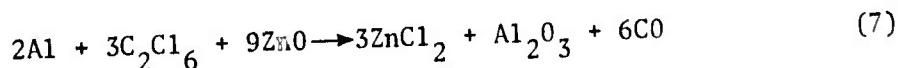
Both of these reaction schemes lead to the same general equation:



The aluminum content is varied in the range 5.5 to 9 percent by weight to regulate the burning time and whiten the resulting smoke. The latter phenomenon may proceed according to the equation



The aluminum content can therefore be reduced to produce a theoretically carbon-free smoke as represented by the equation



During the qualitative analysis, it was demonstrated in the laboratory that the reactions represented by Equations (1), (2) and (4) are initiated at relatively low temperatures under DTA experimental conditions. Also, it has been shown that the reactions represented by Equations (3) and (6) do not initiate at temperatures less than 1000° and 500°C, respectively. The experimental conditions and data from the DTA are shown in Table III.

TABLE III. COMPILED DTA DATA FOR HC SMOKE COMBUSTION

| Expt No. | System | Atm | Mole Ratio | Position of Events ^a , °C | |
|----------|--------------------------------|--------|------------|---|---------------------------------------|
| | | | | Initial Reaction | Reaction Residue |
| 1. | C_2Cl_6 | Ar | | 53 ^{EN} , 76 ^{EN} , 195 ^{EN} | |
| 2. | ^b C_2Cl_6 -Al | Ar | 1:2 | 194 ^{EX} , 271 ^{EX} | ^c 165 ^{EN} |
| 3. | Al_2Cl_6 -ZnO | Ar | 1:3 | 108 ^{EX} | 279 ^{EN} |
| 4. | ^b C_2Cl_6 -Zn | Ar | 1:3 | 304 ^{EX} | 310 ^{EN} |
| 5. | ^b C_2Cl_6 -ZnO | Ar | 1:3 | 306 ^{EX} , ^d 426 ^{EX} | 305 ^{EN} |
| 6. | ^b HC | Ar | | ^e 311 ^{EX} | |
| 7. | ^b HC | CO_2 | | 307 ^{EX} , 392 ^{EX} , 419 ^{EN} | 421 ^{EN} |
| 8. | ^b C_2Cl_6 -ZnO-Al | Ar | 1:3:2 | 314 ^{EX} , 406 ^{EX} | 297 ^{EN} , 415 ^{EN} |
| 9. | ^b C_2Cl_6 -ZnO-Al | Ar | 1:0.4:2 | 278 ^{EX} , 313 ^{EX} | 167 ^{EN} |
| 10. | ^b C_2Cl_6 -ZnO-Al | Ar | 1:0.2:2 | 192 ^{EX} , ^f 293 ^{EX} | 184 ^{EN} |

(a) Superscripts EN and EX indicate endotherm and exotherm, respectively.
 (b) All endothermic events associated with C_2Cl_6 occur at their respective temperatures.
 (c) All binary and ternary mixtures initially containing C_2Cl_6 produce a black material assumed to be carbon.
 (d) Broad exotherm, temperature taken at the approximate maximum point of curve.
 (e) Sample capillary fractured after the maximum of the peak associated with the exothermic event had been passed.
 (f) The experiment was stopped after the first exothermic event, allowed to cool to room temperature, and then reprogrammed to 500°C.

Experiments 2, 3, and 4 of Table III were conducted to establish the initiation temperature and to determine the identity of the products. At least two products, a white crystalline-appearing material and a black material, are formed from the reaction of aluminum and hexachloroethane

(Experiment 2). The white material melts at 165°C and is tentatively identified as Al_2Cl_6 (Lit.m.p.183°C). The black material is assumed to be carbon. Equation (1), therefore, appears to be basically correct. The reaction represented by Equation (2) (Experiment 3 Table III) was found to initiate at 108°C. One of the products exhibits an endotherm at 279°C and is presumed to be impure zinc chloride (Lit.m.p.262°C) or possibly a zinc oxychloride. The product from the reaction of metallic zinc with hexachloroethane exhibits an endotherm at 310°C. The nature of this product was not determined but must be similar to that produced in Experiment 3. Based on this series of experiments it is concluded that the initial steps in the combustion process of HC smoke mixture is best represented by Equations (1) and (2). However, the process represented by Equation (3) may proceed and would then be reinforced by the consumption of zinc by a process represented by Equation (4).

Initial combustion reactions of HC smoke composition material under DTA-type conditions were carried out in crimped stainless steel tubes. Air filled the volume not occupied by solid material. Even though it was not possible to produce an entirely leak-proof system, less than one-third of the hexachloroethane was lost prior to the occurrence of the first exothermic event (311°C). This exotherm was followed by a similar event at 451°C. The similarity of the position of these peaks to those obtained in sealed glass tubes suggests minimal or no participation by the glass in the complicated reaction scheme.

Each thermogram represented in Table III is sufficiently complicated to warrant further study which, however, was beyond the scope of this investigation. The experimental data suggest that the combustion of HC smoke mixture probably involves a variety of complicated reactions.

The following conclusions and observations were apparent from this study and that of Jarvis (Reference 7):

- a. Combustion reaction does not initiate until hexachloroethane, C_2Cl_6 , is in the liquid and/or vapor phase.
- b. The initiating reaction has not clearly been determined. Aluminum reacts with hexachloroethane at the melting/sublimation point of the latter as a binary mixture and up to approximately 5 percent by weight ZnO as a ternary mixture. Beyond 5 percent by weight ZnO , a damping effect appears to take place because the major exothermic event initiates at a higher temperature.
- c. Most of the obvious reactions that may occur during the combustion of HC smoke mixture initiate at temperatures below 500°C, approximately 2000°C below the maximum temperature obtained by Starter Mixture A. The majority of the reactions observed in the laboratory during this study are

exothermic. Therefore, it can be assumed that the overall combustion process is self-supporting once initiated by an energetic starter system in a partially confined environment.

d. Neither the effect of a partial pressure of CO_2 nor the effect of an excessively high pressure on the HC combustion process was clarified.

SECTION X

DISCUSSION AND CONCLUSIONS

It is speculated that the relatively poor performance of the canisters containing the Air Force Armament Laboratory Starter Mixture A is directly related to the absence of the baffle plate. The purpose of the baffle plate is to aid in the canister ejection process, but it was intentionally eliminated from the dynamic projectiles because static testing indicated that the baffle plate partially shielded the canisters from the energy imparted by the expelling charge. This energy, which is required for starter ignition, was also shown to decrease from the nose canister (nearest the expelling charge) to the base canister. Therefore, to provide adequate energy for reliable ignition of the starter material in all three canisters under static conditions, the baffle plate was eliminated.

After the expelling charge functions, the dwell-time of the canisters in the dynamic projectile is greatly increased over that encountered under identical static conditions. In both cases, however, the dwell-time is longer without a baffle plate. This is true because the slightly expanded canisters are seated tightly in the projectile due to the setback forces sustained when the 105mm projectile is fired.

At the time the expelling charge functions, the pressure within the projectile is greatly increased by the formation of nitrogen, carbon monoxide, and carbon dioxide gases. The temperature is also instantaneously increased to some value in excess of that required for starter pellet ignition so the pellets probably ignited within a few milliseconds. The increased pressure and the presence of both gaseous oxides of carbon apparently did not interfere with the ignition and burning characteristics of the starter pellet. It is also probable that the energy imparted to the HC smoke composition by the starter pellet during the dwell-time was sufficient to have caused ignition and sustained reaction.

A differential thermal analysis has demonstrated that major exothermic reactions associated with the functioning of HC smoke composition material are initiated below 500°C. These experiments were carried out in tubes that were sealed initially at a pressure of one atmosphere of air, argon, or carbon dioxide. Once the smoke composition began to burn, thus creating a void in the canister, the pressure differential should have been relieved. It is presumed that the greater pressure existed initially in the projectile cavity and then rapidly equilibrated into the void created in the individual canisters. The effect of a high pressure gaseous mixture of nitrogen and the monoxide and dioxide of carbon on the ignition and burning characteristics of HC smoke composition is not known, but is presumed to be adverse since the initial smoke-trails and overall burn-times were greatly different from those encountered during static firings.

The condition of the canister bases showed that a great amount of heat was generated in that area prior to ejection. Apparently, upon ejection, the softened bases readily expanded outward because of the sudden decrease in pressure and in several cases were ripped open. This condition indicates that a vigorous reaction occurred within the canister prior to ejection and created excess heat and pressure not experienced by a canister in a normally functioning round.

Therefore, the problems encountered during dynamic testing of Starter Mixture A apparently resulted from a combination of factors (listed in order of importance):

1. The absence of the baffle plate in the projectile.
2. The speculated long dwell-time in the projectile.
3. The fast reaction rate of the starter pellet.
4. The adverse burning characteristics of the HC smoke composition due to conditions generated by the first three factors.

SECTION XI

RECOMMENDATIONS

Although the participation of the Air Force Armament Laboratory in the effort to develop an improved starter system for the M1 smoke (HC) canister has ceased, the following recommendations are made should future work be generated using the starter mixes developed during this program.

1. Reincorporate the baffle plate into the system.
2. Continue to thoroughly coat the inner surface of the projectile and the outer wall of the canisters with either Teflon [®] or graphite to aid in canister ejection.
3. Incorporate Starter Mixture B for dynamic testing.

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| 13. ABSTRACT A program was initiated to develop an improved starter system for the M1 smoke (HC) canister used in the 105mm M84A1 (HC) smoke projectile. The experimental starter material was based on an intermetallic-forming reaction of the titanium-boron system. Static and dynamic testing was carried out. The starter system produces the heat necessary to initiate and sustain combustion of HC smoke composition. | | |

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